



## Isotopic record of lead pollution in lake sediments from the northeastern United States

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**Abstract**—Although it is common knowledge that Pb concentrations have increased in lake sediments in the northeastern United States over the last 150 years, the processes responsible have been the subject of debate. In this study, differences in lead isotopic compositions and concentrations in sediment from large lakes (Lake Erie, Ontario, and Michigan) and small ones (Deep Lake and Lake Andrus) are used to infer temporal changes in the source(s) of anthropogenic Pb in the Great Lakes region. A natural (background) component of Pb is present in sediment deposited prior to 1860 in Lake Erie and the other lakes as indicated from low Pb concentrations and uniform lead isotopic compositions. Changes in isotopic ratios of lake sediment reflect differing sources of anthropogenic Pb superimposed on the natural component such as regional deforestation from 1860–1890 followed by coal combustion and ore smelting through 1930. Combustion of leaded gasoline was the dominant anthropogenic Pb source to the atmosphere (and by inference to lake sediment) from 1930–1980. Temporal changes in lead isotopic compositions in lake sediment suggest that the source of the Pb used in gasoline additives gradually changed from 1930 to present. The best example is a distinct shift in lead isotopic ratios in lake sediment deposited after 1970 which corresponds to increased Pb production from the Viburnum Trend deposits in Missouri (present in all lakes except Ontario). However, the changes in lead isotopic compositions are much less variable than and do not parallel those calculated on the basis of annual United States mine production and imports. Rather, anthropogenic recycling of Pb as well as natural mixing processes during emission, transport, and deposition of Pb in lake sediment control most of the variation in lead isotope ratios. Differences in lead isotopic ratios in Lake Michigan, Erie, and Deep Lake sediment preserve regional differences in lead isotopic ratios from U.S. and Canadian sources first noted in aerosols by Sturges and Barrie (1987). More localized sources of Pb (such as point discharges) are needed to explain the results from Lake Ontario and Andrus.

### INTRODUCTION

The anthropogenic addition of Pb to the Earth's ecosystems is recognized on a global scale in Arctic (Sturges and Barrie, 1989b) and Pacific Ocean aerosols (Settle and Patterson, 1982), ice cores from Greenland and Antarctica (Murozumi et al., 1969; Rosman et al., 1993), and corals growing in the Atlantic and Pacific Oceans (Shen and Boyle, 1987); all locations far from pollutant sources. In these studies, differences in isotopic ratios and concentrations of Pb were used to suggest sources for the anthropogenic Pb. However, before the exact provenance of Pb can be identified on a global scale, more must be known about regional and local variations in anthropogenic Pb emissions. One way to tackle this problem is to examine Pb pollution in an area such as the northeastern United States where the history of settlement and economic development is well documented in a now heavily industrialized region. Previous workers used trace element concentrations in lake sediments from this region as a basis to model the emission and deposition of pollutants during the industrialization period (Winchester and Nifong, 1971; Edgington and Robbins, 1976; Nriagu et al., 1979; Griffin and Goldberg, 1983; Eisenreich et al., 1986). In this paper we will demonstrate how the source(s) of a specific pollutant, Pb, can be surmised by use of temporal differences in lead isotopic ratios combined with variations in Pb concentrations in lake sediment.

The lead isotopes used for this purpose are <sup>204</sup>Pb, with no known radioactive parent and those isotopes formed by ra-

dioactive decay having long half lives: <sup>208</sup>Pb from <sup>232</sup>Th, <sup>207</sup>Pb from <sup>235</sup>U, and <sup>206</sup>Pb from <sup>238</sup>U. Identification of Pb source is feasible because sources of natural and anthropogenic Pb to lake sediments have different lead isotopic compositions and lead isotopes are not measurably fractionated during industrial or biological consumption processes (Ault et al., 1970).

Primary natural sources of Pb to lake sediments in the northeastern United States include rock erosion within the catchment basin, and atmospheric inputs from volcanic emissions and dust derived from soil. Addition of Pb from anthropogenic sources may include biomass burning during deforestation; the consumption of fossil fuels including wood, peat, coal, and oil; the mining and smelting of Pb and other metal ores; release of municipal and industrial effluents associated with Pb ore consumption and recycling; and the combustion of leaded gasoline (Nriagu, 1979; Nriagu and Pacyna, 1988). The lead isotopic ratios from many of the anthropogenic and natural Pb sources are available in the literature. When combined with records of land development, fossil fuel use, and Pb ore consumption, lead isotopic ratios and concentrations for anthropogenic emissions can be estimated and compared to those preserved in the sediment record.

To assess the relative importance of atmospheric emissions vs. direct water discharges as sources of anthropogenic lead, we chose sediment samples from basins near the heavily populated and industrialized shorelines of several Great Lakes as well as several small lakes with limited access and undevel-

oped shorelines. It was anticipated that atmospheric emissions would provide a regional Pb distribution and dominate the anthropogenic Pb flux to the small lakes, whereas direct discharges and proximity of industry to the Great Lakes would preserve local, point discharges.

## EXPERIMENTAL METHODS

### Sample Selection

Sediment cores were chosen from Great Lakes basins with well-established, high sedimentation rates which allows the age of sediment deposition to be determined most accurately (Eadie and Robbins, 1987). Cores selected (Fig. 1) included two from the eastern basin of Lake Erie (collected in 1991 and 1988), one from the Rochester basin of Lake Ontario collected in 1991, and one collected from the southeastern basin of Lake Michigan in 1980. After coring, the sediment samples were sectioned, freeze-dried, ground, and stored in either polyethylene or glass vials.  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  were used to date the time of sediment deposition in the Great Lake cores using the analytical method and mathematical formulations described in Robbins (1978) and Robbins and Eadie (1991). The mathematical models of sediment deposition utilized in this study account for variable sedimentation rates, post-depositional sediment mixing, and compaction. Examples of  $^{210}\text{Pb}$  distribution in Great Lakes sediment on which the sediment deposition models are based are reported in Eadie and Robbins (1987).

The sediment from small lakes was obtained from archived material from the PIRLA investigation of recent lake acidification (Whitehead et al., 1990); and included core samples from Lake Andrus (located in the upper peninsula of Michigan) and Deep Lake (located in the Adirondack Mountains in upper New York state) collected in 1984 (Fig. 1). The collection, location, determination of time of sediment deposition, characteristics of the drainage basins, and distribution of trace elements in the sediment cores from the small lakes was described in Kingston et al. (1990), Charles et al. (1990), and Norton et al. (1992). Lake Andrus and Deep Lake are seepage lakes with undeveloped catchments and shorelines.

### Analytical Procedure

Because the purpose of this study was to investigate anthropogenic Pb additions to sediment throughout the Great Lakes region; a procedure was needed to extract the anthropogenic component preferentially from the total Pb contained in the sediment. Shirahata et al. (1980) and Ng and Patterson (1982) demonstrated that the anthropogenic Pb component in sediments can be separated from total Pb by a dilute acid leach. The dilute acid leach will solubilize Pb sorbed to biological debris and ferromanganese films and leave behind residual Pb within the structure of silicate minerals. More elaborate dissolution procedures have been used in other studies to separate the leachable Pb from the more refractory component of Pb. The sequential extraction procedure of Tessier et al. (1979) is commonly used, because it allows operationally defined exchangeable, carbonate-bound, Mn and Fe oxide-bound, organic and residual trace metal components to be determined; and White and Gubala (1990) demonstrated the utility of this digestion procedure on sediment from Deep Lake. The chemicals needed for this procedure, however, are not readily available in the purity needed for analysis of lead isotopic ratios. Instead, extractions were made using quartz- and Teflon-distilled acids (acetic, nitric, hydrofluoric, and hydrochloric) to test acid strength vs. amount of Pb leached on a set of duplicate samples from the same interval of the Lake Erie 1988 sediment core using the following protocol.

Dissolution of sediment samples took place within Class-100 clean rooms. Samples (3–10 mg) were placed in 1.5 ml polypropylene centrifuge tubes and 1 ml of acid was added. The tubes were placed in a closed ultrasonic bath for 90 minutes (the temperature of the acid extract reached 40–45°C). The tubes and contents were allowed to cool overnight, and then centrifuged at 13,000 rpm for 10 minutes the following day.

For determination of lead isotopic ratios, the solution in the centrifuge tubes was separated from the remaining sediment using micropipettes and placed into 15 ml Teflon beakers for subsequent purification. The Pb was separated from other elements using sequential HCl-HBr column chromatography with AG 1X8 anion exchange resin; and loaded onto single, zone-refined Re filaments using phosphoric acid and silica gel. Isotopic ratios were determined by solid-source thermal ionization mass spectrometry using a VG Sector MULTI 1 mass spectrometer equipped with six Faraday collectors.

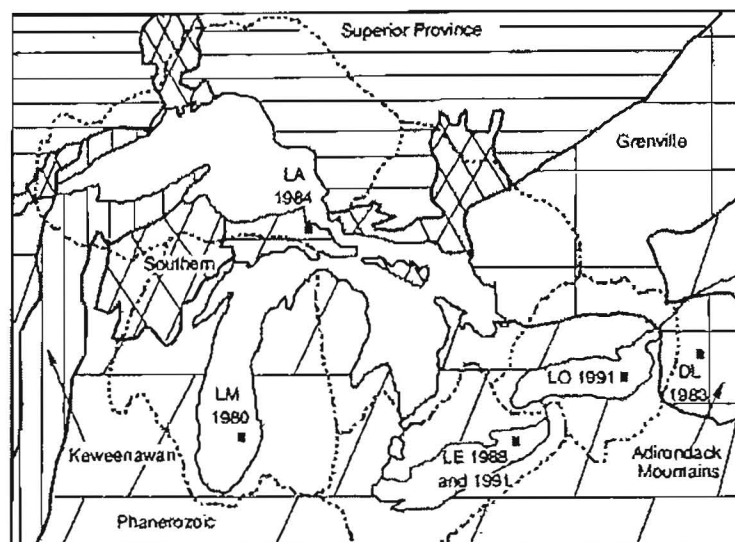


FIG. 1. Location and year of sediment coring superimposed over an outline of the Great Lakes, their drainage basins (stippled lines) and the bedrock geology in the region. The Superior Province is composed mostly of >2.5 Ga granite and greenstone, whereas the 0.9–1.8 Ga Southern, Keweenaw, Grenville, and Adirondack Mtn. regions are composed mostly of granite and metasedimentary rocks: basalt; metasedimentary rocks; and, metasedimentary rocks and anorthosite, respectively. The Phanerozoic rocks (400–500 Ma) consist of sandstone, shales, limestones, and dolomite. Core location key: LA—Lake Andrus LM—Lake Michigan LE—Lake Erie LO—Lake Ontario DL—Deep Lake

Lead analyses were corrected for fractionation (0.11% per a.m.u.) by repeated analysis of the NBS 981 standard. The full procedural blank contained a maximum of 50 picograms of Pb whereas a typical loaded filament contained 200 nanograms of Pb extracted from sediment.

Lead concentrations were determined by ICP-MS (Perkin Elmer model ELAN 5000). Checks on Pb concentrations were made with isotope dilution using a  $^{208}\text{Pb}$  spike (agreement between the two methods was  $\pm 5\%$ ).

As the results in Table 1 demonstrate, the strength and combination of acids used to extract part of the Pb from the samples had little effect on the concentrations and lead isotopic ratios obtained. The Pb concentrations and isotopic ratios obtained are remarkably consistent and indicate that the reservoir containing acid soluble Pb in the sediment was homogeneous. Lead released from the structures of silicate minerals was isotopically distinct from that released from other sites, as indicated from the lead isotopic ratios obtained from the dissolution of the residue with HF. These data do not prove that only anthropogenic Pb is removed during leaching, but does demonstrate that a dilute acid leach releases Pb from different Pb reservoirs than total sediment dissolution. Most of the Pb released by the dilute acid leach of freshwater lake sediments is probably desorbed from iron oxyhydroxide surfaces (Erel et al., 1990; Mantej and Foster, 1991) as demonstrated experimentally by Davis and Galloway (1993) on lake sediment from the Adirondack Mountains.

Based on the results of the leaching study, the 1 N  $\text{HNO}_3$  + 1.75 N HCl acid mixture was chosen to preferentially extract anthropogenic Pb from lake sediment (following the analytical protocol previously outlined). Lead isotopic ratios, concentrations, and mean age of sediment deposition for the intervals of sediment analyzed are presented in Table 2. More samples were analyzed from the Lake Erie cores than the others because the high sedimentation rate in the eastern basin of Lake Erie allowed for the best resolution of time of sediment deposition.

## RESULTS AND DISCUSSION

### Natural Sources of Pb to Lake Sediment

The dominant sources of natural Pb in the Great Lakes region are associated with erosion including direct erosion of glacial deposits and rocks exposed along bluffs and shorelines surrounding the lakes as well as wind blown dust and fluvial inputs from rivers (Kemp and Dell, 1976; Kemp et al., 1977; Ritson et al., 1994). Bedrock geology around and under the Great Lakes basins varies in age and rock type (Fig. 1), as does the thickness and composition of the glacial deposits overlying the bedrock. The rates and type of erosion experienced by the different rock types and glacial deposits affects

the isotopic composition of the Pb incorporated into the lake sediment. Rock erosion resulting in total rock dissolution would release Pb reflecting the history of U/Th/Pb fractionation in the host rocks and their precursors in the Great Lakes region (Fletcher and Farquar, 1977; Franklin et al., 1983; Farquar et al., 1987) as well as Pb produced subsequently from the radioactive decay of Th and U (Dewolf and Halliday, 1991). However, partial rock dissolution could release radiogenic Pb preferentially from metamict U and Th rich minerals resulting in preferential incorporation into lake sediment. Both scenarios result in the incorporation of Pb in sediment with isotopic ratios more radiogenic than those reflecting the time of rock formation (Erel et al., 1990, 1991). Likewise the development of soil incorporates Pb of more radiogenic composition than precursor rock (Chow, 1970; Gulson et al., 1981; Keinonen et al., 1992; Puchelt et al., 1993). This labile, radiogenic Pb can be subsequently incorporated into plants during growth and ultimately be deposited with organic matter in lake sediment.

The isotopic ratios and concentrations of Pb from the 1991 Lake Erie core are remarkably constant prior to approximately 1860 and less so after 1860 (Fig. 2 and Table 2). The constancy of the isotopic ratios and concentrations prior to 1860 probably represents the natural (background) component of leachable Pb in the sediment. This age agrees well with the appearance of *Ambrosia* (ragweed) pollen in other Great Lakes sediment cores (Robbins et al., 1978). The appearance of *Ambrosia* is believed to be associated with settlement in the Great Lakes region, and as such is often used as a marker horizon indicating the start of anthropogenic perturbation of the sediment record. Results from this study indicate additions of anthropogenic Pb to the background component can also be recognized by increased Pb concentrations and changes in isotopic ratios present in all sediment cores.

The lead isotopic ratios of sediment deposited prior to 1860 are slightly different for each sediment core (Table 2) due to different sources and processes which sequester Pb in individual basins. It is not necessary to have similar background lead isotopic ratios in each sediment core in order to quantify anthropogenic Pb additions, rather it must be demonstrated that the background component in the locations from which the cores were sampled is homogeneous. We have done so

Table 1. Sediment Leaching Experiment

Acid Strength	Lead Isotope Ratios					Pb conc. (ppm)
	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	
1N Acetic	2.050	0.8328	18.77	15.64	38.49	20.4
1N HCl	2.051	0.8325	18.78	15.63	38.50	33.2
1N $\text{HNO}_3$	2.052	0.8327	18.79	15.65	38.57	32.9
1.75N $\text{HNO}_3$ + 3N HCl	2.049	0.8318	18.79	15.63	38.51	33.3
6N HCl	2.050	0.8320	18.81	15.64	38.56	32.1
7N $\text{HNO}_3$	2.050	0.8315	18.81	15.64	38.57	32.2
Aqua Regia	2.050	0.8316	18.81	15.64	38.56	32.6
HF Leach of residuum	2.064	0.8378	18.56	15.55	38.30	3.2
2 $\sigma$ Std. Dev	0.002	0.0005	0.02	0.02	0.07	

Each set of measurements was made after leaching 10 mg subsplits of a sample from 40 cm depth from the 1988 Lake Erie Core, except the HF leach, which was the residuum from the aqua regia leach.

Table 2. Measured Lead Isotope Ratios and Concentrations and the Calculated Anthropogenic Only Lead Component from Lake Sediment.

Core and Depth	Year of Sediment Deposition	Lead Isotope Ratios from Dilute Acid Leaches						Pb conc. (ppm)	Calculated Anthropogenic Lead Component						Pb conc. (ppm)
		<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>208</sup> Pb/ <sup>207</sup> Pb	<sup>206</sup> Pb/ <sup>208</sup> Pb	<sup>207</sup> Pb/ <sup>208</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb		<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>208</sup> Pb/ <sup>207</sup> Pb	<sup>206</sup> Pb/ <sup>208</sup> Pb	<sup>207</sup> Pb/ <sup>208</sup> Pb	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	
1991 Lake Erie															
0 cm	1992	2.039	0.8233	18.97	15.66	38.68	23.9		2.047	0.8400	18.60	15.64	38.09	9.1	
1"	1999	2.040	0.8262	18.95	15.65	38.65	28.1		2.048	0.8394	18.62	15.64	38.23	11.0	
10"	1987	2.033	0.8234	18.96	15.66	38.60	41.0		2.034	0.8314	18.82	15.65	38.32	24.1	
14"	1977	2.034	0.8263	18.96	15.64	38.60	44.9		2.037	0.8317	18.83	15.64	38.37	28.3	
18"	1972	2.033	0.8334	18.71	15.63	38.60	61.3		2.040	0.8424	18.54	15.62	38.18	44.3	
24"	1961	2.031	0.8338	19.30	15.63	38.54	58.2		2.053	0.8397	18.45	15.63	38.38	41.4	
30"	1954	2.047	0.8306	18.84	15.63	38.58	43.7		2.055	0.8389	18.44	15.64	38.32	24.9	
34"	1952	2.043	0.8279	18.90	15.63	38.61	34.9		2.049	0.8360	18.70	15.64	38.21	22.1	
38"	1947	2.033	0.8226	19.01	15.66	38.68	37.0		2.033	0.8283	18.81	15.63	38.43	20.2	
42"	1942	2.030	0.8205	19.06	15.67	38.73	34.1		2.026	0.8236	18.99	15.67	38.26	17.3	
46"	1934	2.034	0.8218	19.07	15.68	38.75	21.9		2.032	0.8244	18.97	15.68	38.44	13.1	
50"	1931	2.041	0.8227	19.02	15.64	38.84	29.3		2.049	0.8324	18.83	15.69	38.61	12.3	
54"	1920	2.043	0.8225	19.04	15.64	38.88	13.4		2.040	0.8352	18.72	15.64	38.57	6.8	
62"	1914	2.042	0.8222	19.05	15.67	38.91	24.2		2.039	0.8332	18.80	15.64	38.70	7.4	
64"	1908	2.034	0.8173	19.17	15.67	39.02	18.7		2.043	0.8338	19.18	15.71	39.32	3.9	
74"	1997	2.032	0.8131	19.23	15.69	39.11	18.7		2.007	0.7953	19.04	15.71	40.03	1.9	
82"	1845	2.030	0.8139	19.28	15.69	39.15	17.4		1.911	0.7170	22.44	15.64	43.20	0.6	
90"	1873	2.031	0.8141	19.30	15.71	39.20	19.9		2.013	0.7945	20.02	15.96	40.30	3.3	
Natural Background															
98"	1840	2.034	0.8178	19.18	15.67	39.01	17.3		2.033	0.8174	19.17	15.67	39.00	16.8	
106"	1849	2.032	0.8173	19.17	15.64	38.94	17.1								
114"	1836	2.034	0.8174	19.18	15.67	39.01	16.7								
122"	1824	2.033	0.8172	19.18	15.67	39.03	17.8								
130"	1811	2.033	0.8177	19.18	15.64	38.97	16.7								
138"	1798	2.035	0.8173	19.18	15.67	39.02	17.3								
1988 Lake Erie															
1 cm	1994	2.042	0.8246	18.97	15.68	38.73	23.9		2.043	0.8311	18.64	15.67	37.57	6.7	
5"	1994	2.039	0.8239	18.94	15.64	38.64	23.7		2.050	0.8443	18.44	15.54	37.83	6.3	
10"	1992	2.037	0.8234	18.97	15.67	38.64	32.6		2.041	0.8340	18.74	15.64	38.24	13.2	
15"	1979	2.042	0.8234	18.99	15.63	38.60	33.0		2.051	0.8410	18.39	15.62	38.33	13.8	
20"	1974	2.040	0.8249	18.91	15.64	38.60	29.3		2.049	0.8412	18.54	15.58	37.59	12.1	
23"	1972	2.041	0.8287	18.84	15.63	38.63	30.8		2.030	0.8437	18.47	15.56	37.89	13.6	
30"	1964	2.035	0.8349	18.74	15.63	38.51	40.6		2.071	0.8483	18.43	15.62	38.11	32.4	
40"	1960	2.049	0.8318	18.79	15.63	38.53	22.8		2.044	0.8483	18.37	15.58	37.99	13.6	
50"	1953	2.030	0.8303	18.84	15.64	38.64	34.1		2.047	0.8441	18.33	15.64	38.29	16.9	
70"	1934	2.029	0.8193	19.13	15.64	38.81	29.8		2.022	0.8227	19.03	15.64	38.50	12.4	
90"	1920	2.042	0.8229	19.05	15.67	38.99	25.9		2.040	0.8330	18.31	15.64	38.61	8.7	
130"	1848	2.031	0.8157	19.24	15.69	39.07	24.0		2.024	0.8130	19.42	15.73	39.18	6.8	
Natural Background															
170"	1854	2.033	0.8164	19.20	15.68	39.03	17.2		2.030	0.8164	19.20	15.68	39.03	17.2	
1991 Lake Ontario															
1 cm	1991	2.047	0.8333	18.78	15.68	38.64	104.1		2.047	0.8343	18.70	15.68	38.29	83.4	
3"	1979	2.047	0.8332	18.76	15.67	38.68	124.1		2.047	0.8376	18.70	15.64	38.63	103.4	
10"	1964	2.043	0.8292	18.90	15.68	38.64	47.3		2.044	0.8318	19.23	15.67	38.51	46.4	
15"	1943	2.054	0.8273	18.55	15.69	38.52	40.0		2.042	0.8323	18.82	15.68	38.35	19.3	
20"	1922	2.033	0.8141	19.32	15.73	39.28	33.9		1.977	0.7749	20.32	15.87	40.34	3.1	
25"	1895	2.022	0.8049	19.31	15.74	39.45	22.6		1.720	0.6054	24.83	16.18	44.73	1.7	
30"	1843	2.034	0.8167	19.24	15.71	39.37	21.4		1.720	0.6174	24.22	16.23	44.01	0.7	
Natural Background															
50"	1730	2.044	0.8232	19.04	15.69	38.99	20.9		2.047	0.8235	19.07	15.70	39.01	20.7	
70"	1630	2.048	0.8237	19.04	15.70	39.03	20.3								
1980 Lake Michigan															
1.3 cm	1980	2.022	0.8203	19.12	15.69	38.63	81.8		2.027	0.8244	19.01	15.67	38.54	69.5	
3.0"	1976	2.032	0.8233	19.04	15.71	38.68	101.7		2.034	0.8290	18.94	15.71	38.60	89.4	
4.3"	1971	2.033	0.8278	18.93	15.67	38.69	104.1		2.039	0.8314	18.83	15.63	38.59	99.8	
9.3"	1952	2.030	0.8265	18.97	15.64	38.56	101.9		2.039	0.8304	18.84	15.67	38.64	89.6	
14.0"	1932	2.021	0.8172	19.19	15.68	38.78	70.3		2.027	0.8212	19.04	15.67	38.68	37.8	
19.0"	1910	2.033	0.8194	19.15	15.70	38.94	35.4		2.034	0.8304	18.83	15.67	38.78	21.3	
28.0"	1843	1.947	0.7849	20.09	15.77	39.33	16.3		1.901	0.7449	21.18	15.84	40.34	4.1	
Natural Background															
34.0"	1805	1.990	0.7964	19.72	15.74	39.24	11.3		1.990	0.7963	19.72	15.73	39.23	12.3	
36.0"	1745	1.990	0.7964	19.72	15.74	39.24	11.3								

for the Lake Erie cores, because sediment deposited prior to 1860 in the 1991 core as well as those obtained from the 1988 core (obtained from approximately the same location) have lead isotopic ratios within analytical uncertainty of one another (Table 2). We have assumed that the background Pb component in the other lakes is as homogeneous as that in Lake Erie.

#### Calculating the Anthropogenic Component of Pb from the Total Pb Leached

The natural Pb component can be subtracted from the total Pb leached to calculate the amount and isotopic composition

of anthropogenic Pb added to the background. Using Lake Erie as an example, this is accomplished by subtracting the Pb concentration and isotopic composition of the background Pb component (the average of the six values from the sediment deposited prior to 1860) from the sediment deposited after 1860. The mathematical formulation follows that of Shirahata et al. (1980) and Ng and Patterson (1982). Using  $^{207}\text{Pb}/^{206}\text{Pb}$  as an example,

$^{207}\text{Pb}/^{206}\text{Pb}$  Anthropogenic Pb component

$$= ((^{207}\text{Pb}/^{206}\text{Pb TL})(\text{ppm Pb TL})$$



Table 2. (Continued)

1984 Lake Andrus												
0.5 cm	1984	2.043	0.8204	18.81	15.43	34.43	199.7	2.044	0.8316	18.78	15.42	34.40
2.5 "	1972	2.048	0.8320	18.79	15.44	34.49	174.7	2.050	0.8354	18.74	15.43	34.43
3.0 "	1960	2.050	0.8351	18.87	15.72	34.49	132.7	2.053	0.8347	18.83	15.72	34.45
7.5 "	1945	2.049	0.8331	18.50	15.64	34.52	91.3	2.053	0.8342	18.73	15.63	34.45
10.0 "	1930	2.079	0.8173	19.18	15.48	34.92	70.0	2.072	0.8191	19.12	15.44	34.44
15.0 "	1910	2.073	0.8214	19.04	15.45	34.73	15.3	2.057	0.8351	18.55	15.51	34.19
20.0 "	1990	2.053	0.8214	19.04	15.44	34.70	13.6	2.042	0.8380	18.44	15.47	34.05
25.0 "	1970	2.024	0.8173	19.19	15.44	34.87	11.3	2.059	0.8340	18.30	15.41	34.10
35.0 "	1935	2.007	0.8070	19.49	15.73	39.12	7.1	2.059	0.8379	17.97	15.10	37.10
Natural Background												
45.0 "	1750	1.994	0.8002	19.83	15.87	39.37	3.9	1.994	0.8002	19.82	15.87	39.37
1983 Deep Lake												
0.5 cm	1992	2.079	0.8312	18.76	15.59	34.24	429.4	2.038	0.8316	18.74	15.58	34.19
2.5 "	1976	2.054	0.8379	18.64	15.62	34.24	321.0	2.055	0.8387	18.42	15.62	34.24
4.0 "	1971	2.051	0.8405	18.52	15.57	34.12	343.3	2.059	0.8413	18.50	15.57	34.08
6.5 "	1960	2.055	0.8380	18.57	15.54	34.16	259.5	2.054	0.8397	18.53	15.56	34.07
8.5 "	1947	2.049	0.8324	18.74	15.60	34.34	227.8	2.049	0.8343	18.70	15.60	34.20
10.5 "	1932	2.050	0.8327	18.72	15.59	34.39	194.8	2.051	0.8345	18.68	15.59	34.23
12.0 "	1905	2.046	0.8263	18.27	15.59	34.41	12.7	2.048	0.8329	18.78	15.58	34.39
16.0 "	1871	2.016	0.8099	19.51	15.48	39.28	34.4	1.989	0.7904	19.90	15.74	39.33
Natural Background												
24.5 "	1790	2.040	0.8161	19.16	15.83	39.33	19.2	2.040	0.8161	19.14	15.83	39.33

$$- (^{207}\text{Pb}/^{206}\text{Pb BC})/(\text{ppm Pb BC})$$

$$- \text{ppm Pb BC},$$

where TL = total leach and BC = background component.

The values for the anthropogenic Pb component for all sediment cores are presented in the right half of Table 2, and were calculated using the background (natural) Pb values for each individual core. The calculated anthropogenic isotopic ratios of Pb are sensitive to the precision of the Pb concentrations, especially when there is little difference between the total Pb leached and the background component. In such cases the error bars on the calculated anthropogenic component will be much larger than when the amount of anthropogenic component of lead is many times greater than the background component. Nonetheless, the calculated anthropogenic component, rather than the total leached, is the value needed in order to constrain Pb sources most accurately.

For example, the time traces of lead isotopic ratios in  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$  space for the total and anthropogenic only Pb components in Lake Erie sediment have similar trends (Fig. 3). However, by subtracting the background component, the isotopic ratios of the anthropogenic component alone can be better resolved. The trends in the anthropogenic Pb component in Lake Erie sediment indicate that shortly after 1860 the anthropogenic Pb component was from sources more thorogenic than the background (higher  $^{208}\text{Pb}/^{206}\text{Pb}$ ). Around the turn of the century until 1920 there were additions from a source less radiogenic than the background component. In the early 1930's to 1940's there was a trend toward lower  $^{207}\text{Pb}/^{206}\text{Pb}$  with constant  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios. This was followed by a trend paralleling that at the turn of the century but with lower  $^{208}\text{Pb}/^{206}\text{Pb}$  for a given  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio. There was an abrupt change in isotopic ratios after 1972, and another after 1980.

The background and anthropogenic Pb components from the other lakes are presented in Fig. 4. A convention of  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$  was chosen to examine variations in all of the lead isotopes on the same plot. However, any set of isotopic ratios could be plotted against one another and result in similar resolution of the anthropogenic Pb component. Before discussing the differences and similarities in these trends

in detail, the identification of possible anthropogenic sources of Pb using isotopic ratios will be explained.

#### Anthropogenic Sources of Pb to Lake Sediment

The dominant source of anthropogenic Pb to lake sediment is believed to be from the atmosphere (Nriagu, 1978; Nriagu and Pacyna, 1988). It is known that Pb has a short residence time in the water column of the Great Lakes and is quickly transported to lake sediments in association with particulate scavenging processes (Jaffe and Hites, 1986; Eadie and Robbins, 1987). Therefore, the sources of anthropogenic Pb added to lake sediments should have a close relation in time and quantity to atmospheric emissions of Pb. The temporal sources of Pb emitted to the atmosphere can be predicted from historical records which document the consumption of fossil fuels, as well as the production of Pb from domestic and foreign ore deposits, and use of Pb in gasoline additives. The consumption records for these commodities are available by year in publications including *Historical Statistics of the United States*, *United States Department of the Interior Bureau of Mines Mineral Resource Yearbooks* and *Mineral Commodity Summaries*, and *Yearbooks of the American Bureau of Metals Statistics*. The computation of Pb emissions from these sources to the atmosphere can be estimated with the following caveats: (1) the amount of Pb within wood, coal, and oil prior to and after combustion is variable, (2) the amount of Pb emitted to the atmosphere after fossil fuel burning or ore smelting is dependent upon the type of pollution control measures used (Winchester and Nifong, 1971; Ondov et al., 1979; Smith et al., 1987), and (3) the distance that Pb travels from emissions sources such as smelters or coal-fired power plants is still being ascertained (Rabinovitz and Wetherill, 1972; Gulson et al., 1981; Pacyna, 1986; Ohlander et al., 1993) because the transport of aerosols containing Pb is a function of particle size, chemistry, atmospheric conditions such as prevailing wind velocity and direction, as well as mode and duration of precipitation (Pacyna, 1987).

The Pb concentration in coal from the United States ranges from 3–55 ppm (National Research Council, 1980). The Pb content of wood is not as well known. From studies of coal

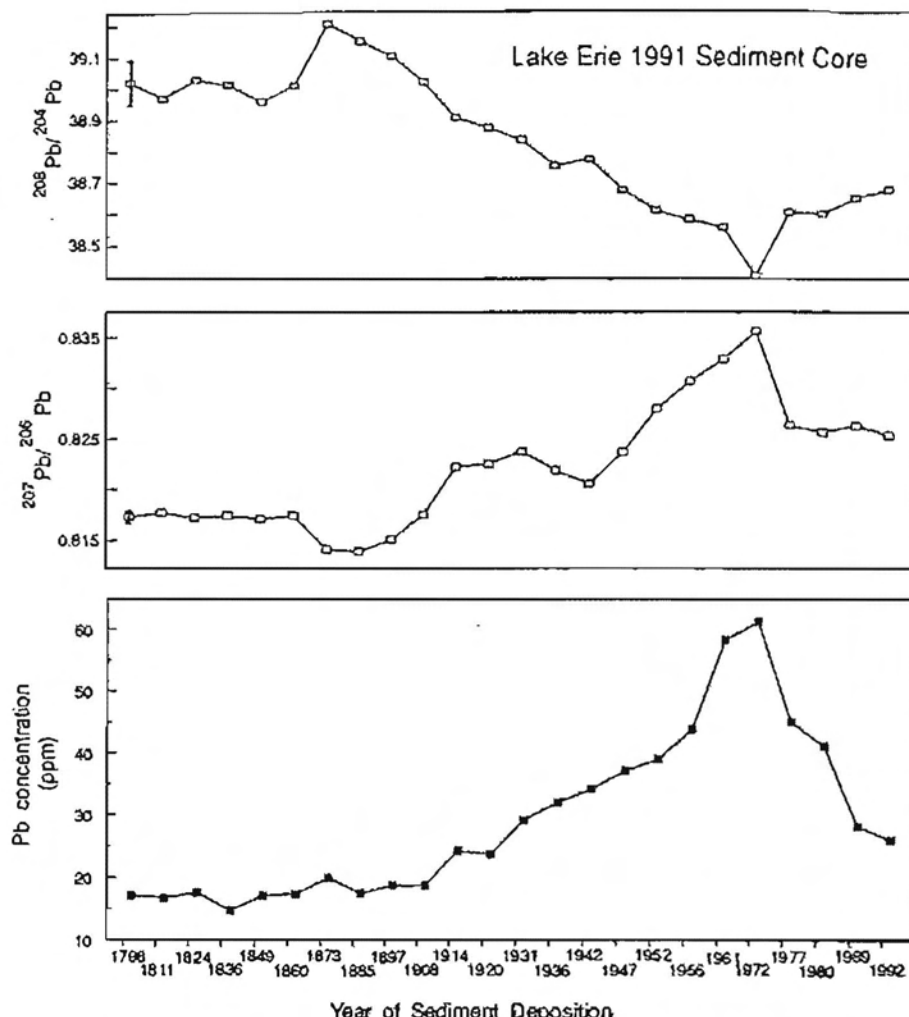


FIG. 2. Temporal changes in lead isotopic ratios and concentrations obtained from dilute acid leaches of sediment from the Lake Erie 1991 core. Two sigma error bars are superimposed over the data from sediment deposited in 1798.

combustion, it is known that Pb is concentrated in fly ash relative to bottom ash, with smaller particles containing the highest Pb concentrations (National Research Council, 1980; Pacyna, 1987). The emission of Pb associated with wood burning has not been studied in the same detail, but should behave in a similar manner. Before pollution controls were mandated in the Clean Air Acts much of the original Pb contained in the coal or wood would have been directly emitted to the atmosphere via fly ash. For the source emission calculations in this study, emissions to the atmosphere of 3.5 ppm of Pb per ton of wood burned (Pacyna, 1986) and 4.5 ppm of Pb per ton of coal combusted (Nriagu, 1979) were used.

Lead emissions associated with ore production include that from fugitive dust during mining and subsequent concentration processes as well as smelter emissions during metal production. Emission levels from smelters depends on pollution control technology. Modern day smelters emit little Pb to the atmosphere (less than 0.14% in best cases); but the potential loss from production to finished product is as much as 12% (Smith et al., 1987). For this study, 0.5% of the total Pb produced during the production process was estimated to be emitted to the atmosphere.

Estimates of emissions of Pb directly to the atmosphere during gasoline combustion range from 50–66% of the original Pb concentration in the gasoline (Fachetti, 1989). The rest is retained within the exhaust systems of the vehicles. An emission estimate of 66% was used in this study.

Estimates of the emissions of Pb to the atmosphere from wood and coal burning, ore production, and consumption of gasoline for the entire United States as a function of time are shown in Fig. 5. From Fig. 5, the predominant anthropogenic Pb source of lead emitted to the atmosphere from 1850–1880 should have been the burning of wood, from 1880–1930 there were approximately equal contributions from coal and ore smelting, and after 1930, Pb emissions from the combustion of gasoline far outweigh the other sources.

#### Anthropogenic Sources of Pb in Lake Erie Sediment

If the anthropogenic component of Pb in Lake Erie sediment is now reexamined, (Figs. 2 and 3) the magnitude of the changes in Pb concentrations mirrors the addition of Pb to the atmosphere predicted in Fig. 5. Distinct changes in isotopic ratios accompany the changes in Pb concentrations in the lake

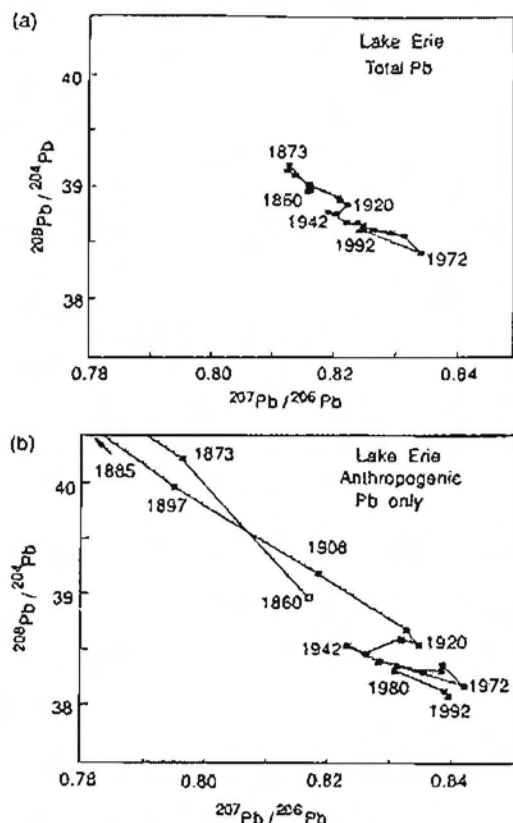


FIG. 3. (a) The isotopic ratios of the total (anthropogenic + natural) lead obtained from a dilute acid leach of sediment from the 1991 Lake Erie core. Data labels correspond to the year of sediment deposition. (b) The isotopic ratios of the anthropogenic lead component calculated by subtracting the natural (background) lead component from the total lead isotopic ratios. The data point labeled 1860 corresponds to the natural lead component.

sediments. For example, slight increases in concentrations and major departures in isotopic compositions of Pb occurred during the time when Pb emissions from wood burning should have been the predominant source of lead to lake sediment, followed by further increases in Pb concentrations and shifts in isotopic ratios when coal and ore smelting predominated, followed by major increases in Pb concentration and changes in isotopic ratios after 1930 corresponding to the use of Pb in gasoline. Do the changes in isotopic ratios correspond to changes in the sources of Pb emitted to the atmosphere? As a test, the lake sediment data are superimposed over lead isotopic ratios from literature values for coal and ore deposits (Fig. 6a and b). No equivalent dataset of lead isotopic compositions for wood is available.

Prior to 1900 lead isotopic ratios of Lake Erie sediments do not plot over values defining the coal or ore fields (Fig. 6a and b). The most logical explanation for the anthropogenic component of the lead isotopic ratios of sediments prior to 1900, are processes resulting from deforestation in the Great Lakes region. Historical records attest to the importance of timbering to local economies at this time and detail the occurrence of major forest fires in the Great Lakes region as well. The appearance of *Ambrosia* pollen (Robbins et al.,

1978) and charcoal derived from wood burning (Goldberg et al., 1981) are supporting evidence for deforestation in sediment cores. Whether the changes in Pb concentration and isotopic ratios reflect burning of biomass or increased erosion rates due to land denudation is more difficult to assess.

From 1900 to 1920, lead isotopic ratios from Lake Erie sediment cross the range in values from West Virginia coal and plot near those of coal from Pennsylvania (Fig. 6b). These states were the predominant sources of coal in the U.S. during this time. Supporting evidence for Pb in lake sediment from a coal source includes charcoal fragments from coal burning found in other sediment cores from the Great Lakes region during this period of time (Goldberg et al., 1981; Dell and Booth, 1977). Because the lead isotopic ratios in lake sediment are close to, but do not directly overlap with those of coal, an additional source of Pb is needed. The production and consumption of Pb ore by industry is a likely source (Fig. 5) for this additional component of anthropogenic lead.

The temporal production and use of Pb by industries in the United States is fairly well documented. Missouri has almost always been the leading state in terms of Pb production. However, several mining districts have produced Pb at different times in Missouri, and the Pb from the different districts has different averages and ranges in lead isotopic compositions (Fig. 6a). In addition to domestic production, the United States has imported known quantities of Pb from other countries (Fig. 7). From the United States domestic production and import records, a prediction of overall change in isotopic ratios of lead consumed over time can be calculated. This entails combining the Pb mining production and import records from individual states and foreign countries for every year from the 1880s to present with literature values of lead isotope ratios from mining districts to produce a prediction of the yearly, weighted, average isotopic composition of Pb consumed (Graney, 1994).

A smoothed version of the estimated yearly variation in lead isotopic ratios based on ore production records is superimposed over the Lake Erie sediment data in Fig. 8a. Overall, the variation in lead isotopes from the lake sediment is less than predicted from ore production and consumption records. Prior to 1942, agreement between the trends is minimal; indicating that either Pb emitted from the burning of fossil fuel dominates the anthropogenic component of Pb in the sediments, or contributions of anthropogenic lead during ore processing are regional rather than national in scope. After 1942, the general trends in the Pb production and sediment record are in the same direction but are offset from one another. The combination of increased Pb production from the New Lead Belt in combination with its unusual lead isotopic composition controls much of the overall change in the calculated lead isotopic ratios after 1961. A major turnaround in the lead isotope ratios from the sediment record occurs after 1972, rather than the prediction of 1961 from ore consumption records. Reasons for the differences between the predicted lead isotopic composition and that found in lake sediment become more apparent after the results from the other cores are examined.

#### Comparison of Lead Isotopic Ratios between Sediment Cores

The lead isotopic ratios of Lake Michigan sediment are similar to those from Lake Erie (Figs. 3 and 4) at the times